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Stanley L./Ruby,
Tobin J./Marks

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ON THE STRUCTURE OF STARCH-IODINE

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Abstract

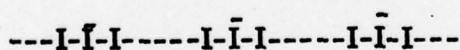
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The structure of the blue-black iodine complex of amylose (the linear, helical component of starch) has been studied by resonance Raman and iodine-129 Mössbauer spectroscopy. It is concluded from these studies and parallel work on selected model compounds that the predominant polyiodide present is I_5^- .

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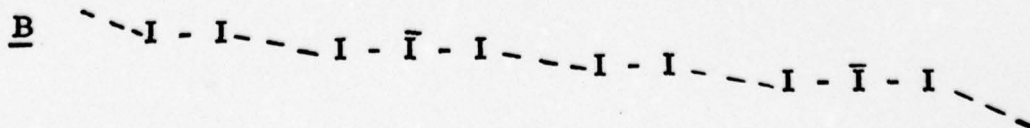
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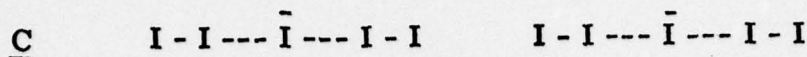
It has been known for many years that the linear, helical component of starch, amylose, forms an intensely blue-black adduct with iodine in the presence of iodide.¹ The pioneering spectral and X-ray diffraction investigations of Rundle and co-workers² established that the iodine atoms are present in a one-dimensional chain within the amylose helix (arrayed in a periodicity probably incommensurate with the pitch of the helix) and give rise to the intense optical absorption ($\lambda_{\text{max}} \approx 600 \text{ nm}$).² The exact structural nature of the polyiodide chromophore has been the subject of considerable study and speculation. For example, it has been proposed that the iodine is present as discrete I_2 units,^{3a} "dissolved" in the hydrophobic interior of the helix, and also that iodine is present as linear chains of I_3^{-1} (A) ions



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as in $(\text{benzamide})_2\text{H}^+\text{I}_3^{-4}$. In addition, studies of related cyclohexaamylose complexes⁵ suggest the possibility of arrays of alternating I_2 and I_3^{-} units (B) or symmetrical I_5^{-} species (C). Despite





the application of a variety of physical techniques to this problem,⁶ it has not been possible to differentiate among these structures and to provide definitive information on the identity of the polyiodide species present in starch-iodine. We have recently shown that the combination of resonance Raman⁷ and iodine-129 Mössbauer spectroscopy,⁸ aided by studies of appropriately selected model compounds, is a powerful tool for elucidating polyiodide structure in low-dimensional mixed valence materials.⁹ In this communication we apply these techniques to the starch-iodine problem. We provide unambiguous evidence that the predominant polyiodide species within the amylose helix is I_5^- .

In Figure 1 are presented resonance Raman scattering spectra (5145Å excitation, spinning samples) of the amylose iodine complex (prepared in deionized water from potato amylose, I_2 and KI, washed with deionized water, and freeze-dried)¹⁰ and several key model compounds of known structure. In general, only totally symmetric normal vibrational modes (and the corresponding overtones and combinations) exhibit appreciable intensity in polyiodide resonance Raman spectra.⁹ The observed I-I stretching frequencies reflect the tendency of I_2 to act as an electron acceptor and of electron donors (e.g. I^-) to lower the I-I bond order.^{9a, 11} Thus, coordination of I^- to I_2 producing I_3^- , lowers the I-I stretching frequency from 207 cm^{-1} to 128 cm^{-1} (the

average of the Raman-active totally symmetric stretch at 108 cm^{-1} and the infrared-active antisymmetric stretch at 148 cm^{-1} ¹²). As can be seen in Figure 1A, starch-iodine exhibits strong scattering at 163 cm^{-1} , and very weak scattering at 109 and 56 cm^{-1} ; overtones and combinations are also observed.¹³ This spectrum differs sharply from those of I_2 in benzene (Figure 1C, $\nu_{\text{fundamental}} = 207\text{ cm}^{-1}$) alcohols or ethers,¹⁴ (benzamide)₂ H^+I_3^- (Figure 1D, $\nu_{\text{I}_3^- \text{ symm, fundamental}} = 108\text{ cm}^{-1}$), which has structure A⁴, and either (phenacetin)₂ $\text{H}^+\text{I}_3^- \cdot \text{I}_2$ ^{15a} (Figure 1E $\nu_{\text{I}_2} = 187\text{ cm}^{-1}$, $\nu_{\text{I}_3^-} = 120\text{ cm}^{-1}$)^{15b} or (α -cyclohexaamylose)₂ $\cdot \text{Li}^+\text{I}_3^- \cdot \text{I}_2 \cdot 8\text{H}_2\text{O}$ ⁵ (Figure 1F, $\nu_{\text{I}_2} = 173\text{ cm}^{-1}$, $\nu_{\text{I}_3^-} = 110\text{ cm}^{-1}$)^{15b} which have structure B. On the other hand, compounds with chains of I_5^- ions (structure C) exhibit a spectrum essentially identical to that of the starch compound. Thus, (trimesic acid $\cdot \text{H}_2\text{O}$)₁₀ H^+I_5^- ¹⁶ (Figure 1B) exhibits strong scattering at 162 cm^{-1} and weaker bands at 104 and 75 cm^{-1} .^{15b} The 162 cm^{-1} transition is reasonably assigned to a fundamental normal mode involving the symmetrically coupled internal stretching of the two " I_2 " units.¹⁷ That the force constant is perturbed less from free I_2 than in I_3^- reflects the fact that the available electron density of the I^- donor must now be distributed between two I_2 acceptors.

It is known² that the blue-black amylose complex can also be prepared from iodine vapor and amylose which has been crystallized from butanol. We find the resonance Raman spectrum of this material to be identical to that of the complex prepared in aqueous solution from

I_2 and I^- . It has been previously suggested¹⁸ that hydrolysis of I_2 produces I^- in the crystalline amylose.

In order to investigate the possible presence of Raman-inactive I^- and to add further weight to the I_5^- proposal, iodine -129 Mössbauer studies were undertaken. The amylose-iodine adduct was prepared by the aqueous procedure described above, using ^{129}I . The Mössbauer spectrum at 4°K is shown in Figure 2A, along with the best computer fit to the experimental data. Data analysis techniques are described elsewhere.¹⁹ The spectrum is best fit to a model with three inequivalent iodine sites in approximate relative populations of 2:2:1. Derived site population, isomer shift, and quadrupole splitting parameters are presented in Table I. Importantly, attempts to constrain the model to 1:1:1 site populations (as in CsI_3) or to two sites in a ratio of 2:1 (as in $(benzamide)_2H^+I_3^-$) produced a precipitous deterioration in the goodness of fit parameter. There is no evidence of I^- ($\delta = -0.51$ mm/sec, $e^2qQ = 0^8$) in the spectrum and it is estimated that this species is present in less than 3 mole percent. For comparison to the amylose data, the Mössbauer spectrum of $(trimesic\ acid \cdot H_2O)_nH^+I_5^-$, enriched in ^{129}I , is shown in Figure 2B. The parameters obtained from the optimum fit are set out in Table I. The derived site populations give an indication of the accuracy of the analysis. These numbers as well as the isomer shift and quadrupole splitting parameters are in close agreement with the amylose-iodine data, and provide further support for the pentaiodide structure.

Besides providing information on a long-standing problem, this work further illustrates the power of the resonance Raman/iodine Mössbauer technique for elucidating the structures of unusual polyiodides. Application to a variety of disordered, noncrystalline, or microcrystalline electronic and optical materials is particularly promising.

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13. Overtones are assigned at $322 (2 \times 163)$ and $214 (2 \times 109) \text{ cm}^{-1}$; the band at $272 (163 + 109) \text{ cm}^{-1}$ is assigned to a combination. The presence of a combination transition can be taken as evidence that the contributing species are not in separate lattices (i. e. that the spectrum is not due to a mixture of compounds).
14. a. Coordination of oxygen donors^{14b} such as are present near the interior of the amylose helix⁵ produces only a small shift in the I-I stretching frequency, viz., $\nu_{\text{fundamental}}$ (diethyl ether) = 204 cm^{-1} and $\nu_{\text{fundamental}}$ (n-butanol) = 197 cm^{-1} .
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21. Camille and Henry Dreyfus Teacher-Scholar

Table I
Iodine -129 Mössbauer Parameters

<u>Compound</u>	<u>Amylose - Iodine</u>	<u>(Trimesic Acid·H₂O)₁₀H⁺I₅⁻</u>
<u>Site 1</u>		
$\delta(\text{mm/sec})^a$	1.22(2)	1.15(3)
$e^2qQ(\text{MHz.})^b$	-1743(3)	-1777(5)
$\Gamma(\text{mm/sec})^c$	1.14(4)	1.15(5)
Relative population	1.90(10)	1.96(10)
<u>Site 2</u>		
$\delta(\text{mm/sec})$	0.53(3)	0.53(5)
$e^2qQ(\text{MHz.})$	-1187(8)	-1404(8)
$\Gamma(\text{mm/sec})$	2.13(8)	1.75(5)
Relative population	1.82(10)	1.78(10)
<u>Site 3</u>		
$\delta(\text{mm/sec})$	0.14(2)	0.13(5)
$e^2qQ(\text{MHz.})$	-842(5)	-965(5)
$\Gamma(\text{mm/sec})$	1.08(5)	1.04(4)
Relative population	1.00	1.00

^aVersus ZnTe

^bFor ¹²⁹I

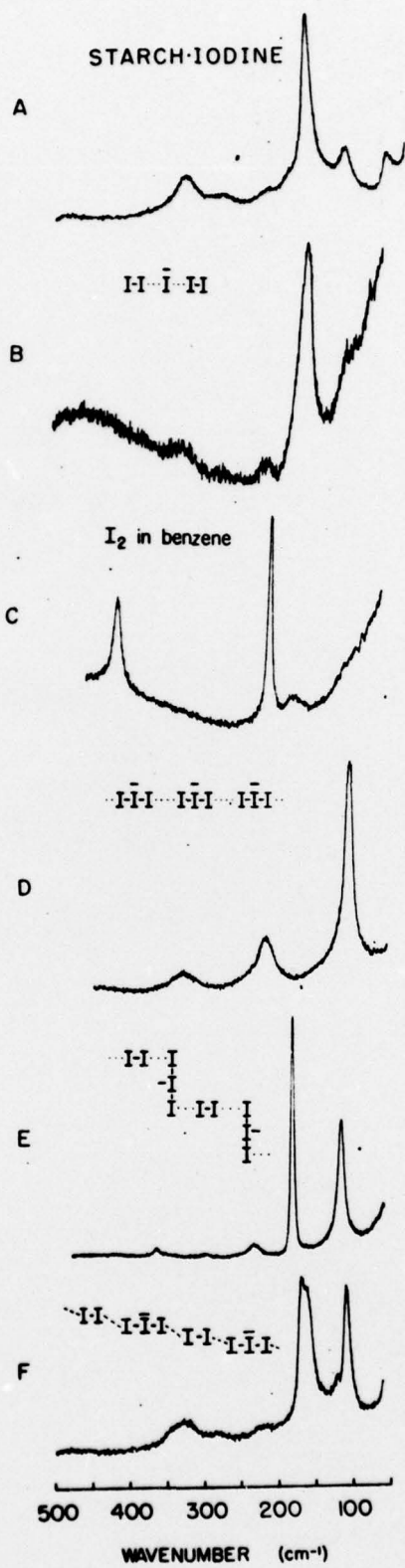
^cLinewidth

Figure Captions

Figure 1. Resonance Raman spectra (5145Å excitation) of A. Starch(amylose) iodine, B. Polycrystalline(trimesic acid · H₂O)₁₀H⁺I₅⁻, C. I₂ dissolved in benzene, D. Polycrystalline (benzamide)₂H⁺I₃⁻, E. Polycrystalline (phenacetin)₂H⁺I₃⁻ · I₂, F. Polycrystalline (α - cyclohexaamylose)₂ · Li⁺I₃⁻ · I₂ · 8H₂O.

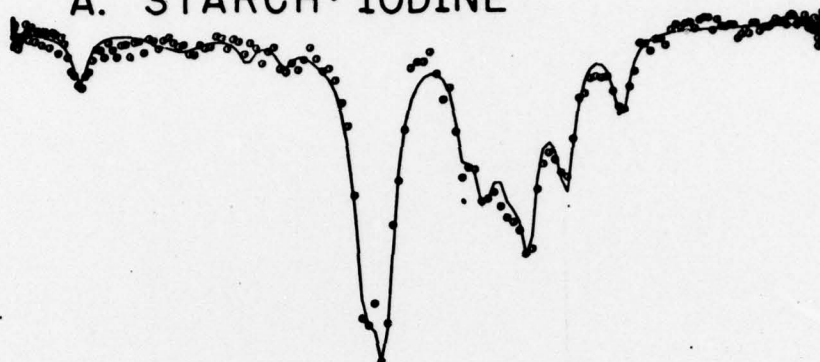
Figure 2. Iodine -129 Mössbauer spectra of the indicated compounds at 4° K. The solid lines represent the best computer fit to the experimental data points.

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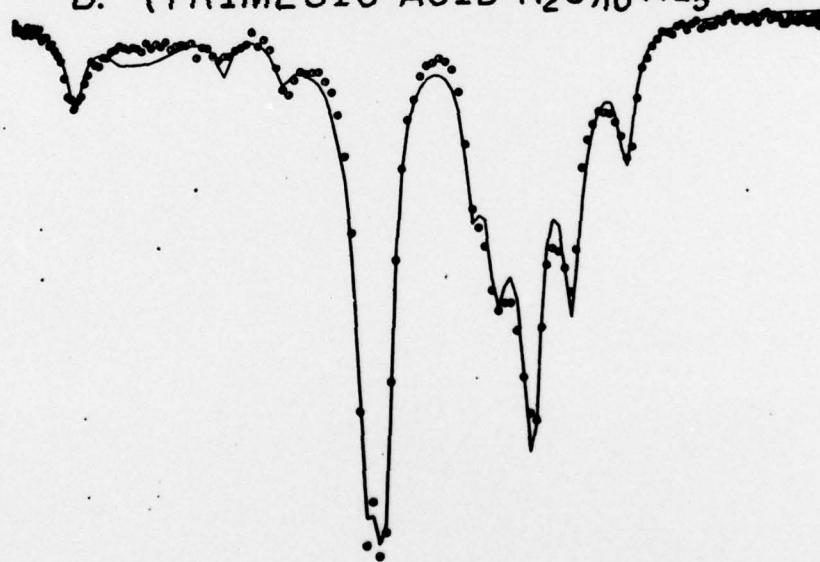


^{129}I MÖSSBAUER SPECTRA

A. STARCH · IODINE



B. $(\text{TRIMESIC ACID} \cdot \text{H}_2\text{O})_{10} \cdot \text{HI}_5$



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